Negative isotope effect of a BCS-like gap; an inelastic light scattering study

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In a prior study of the boron isotope effect on the transition temperature (T_c) of RNi$_2$B$_2$C (R = Y, Lu) system, a positive isotope effect was observed, e.g., $T_c(^{10}B) > T_c(^{11}B)$. BCS theory predicts that the superconducting gap at zero temperature (Δ_0) is proportional to T_c. Therefore, the gap should also show a positive boron isotope effect. On the contrary, in an inelastic light scattering study, we report a negative boron isotope effect on the energy Ω of the gap-like feature in B_{2g} symmetry, e.g., $\Omega(^{10}B) < \Omega(^{11}B)$. The origin of the effect is discussed in terms of selective probing of a non-conventional electron-phonon interaction on part of the Fermi surface, probably near the X point in the Brillouin zone.

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In a previous study of an isotope effect on the transition temperature (T_c) of RNi$_2$B$_2$C (R = Y, Lu) system,[1] positive isotope exponents $\alpha_B^{Tc} = +0.21 \pm 0.07$ for YNi$_2$B$_2$C and $+0.11 \pm 0.05$ for LuNi$_2$B$_2$C were observed upon changing the mass of the boron site. The exponent α_B^{Tc} is defined as $\alpha_B^{Tc} \equiv -\frac{\Delta \ln T_c}{\Delta \ln M_B}$. A relatively large positive value despite the light mass of boron is regarded as a good indication that these materials are BCS-type superconductors, where phonons involving boron atoms play a major role in the pairing mechanism.

BCS-type theory predicts that the superconducting gap in the limit of the absolute zero temperature (Δ_0) is proportional to T_c. In weak coupling $\Delta_0 = 1.76 k_B T_c$, where k_B is the Boltzmann constant. The gap should also show a positive isotope effect upon changing the boron mass. We report here the contrary result: In an inelastic light scattering study, we observe a negative isotope effect of the gap-like Raman peak in B_{2g} symmetry.

The gap Δ can be measured by electronic Raman scattering. The photon scattering process excites two quasiparticles out of the condensate at a minimum energy cost of 2Δ. In the limit of small wave-vector transfer q relative to the inverse coherence length and small elastic and inelastic scattering rate relative to $2\Delta/\hbar$ and with neglect of final state interactions, the Raman spectrum has a peak at an energy shift of 2Δ. Earlier measurements on $NbSe_2$ and A15 compounds showed redistribution of the continuum of the Raman spectra and the formation of a 2Δ-like peak upon cooling the samples below T_c.[2] Electronic Raman studies have played important role in characterizing the nature of the superconducting gap of the high-temperaure superconductors.[3]

Compared with other techniques that measure the gap, such as tunneling and photoemission spectroscopy, inelastic visible light scattering has the advantage of measuring the anisotropy of the gap while being less surface sensitive.

The single crystal samples were grown by the flux-growth method[4, 5] and were characterized by resistivity, magnetization, and neutron scattering.[6] RNi$_2$B$_2$C crystalizes in the tetragonal body-centered space group $I4/mmm$, and phononic Raman analyses have been made earlier.[7] Here, we concentrate on the electronic Raman scattering from the quasi-particles in normal and superconducting states.

Raman spectra were obtained in a pseudo-backscattering geometry using a custom-made subtractive triple-grating spectrometer designed for very small Raman shifts and ultra low intensities.[8] A 3 mW beam of 6471 Å Kr-ion laser light was focused onto a spot of $100 \times 100 \mu m^2$. The temperature rise ΔT of the focal spot above ambient temperature was estimated by solving the heat-diffusion equation. ΔT is largest at lowest temperature because of the smaller values of the thermal conductivity.[9] The estimated ΔT is 2.7K at 4K and 0.9K at 14K for YNi$_2$B$_2$C single crystals. The ambient temperature at which the Raman continua begin to show the redistribution was determined to be 14K, in agreement with this estimate. The spectra were corrected for the Bose factor and therefore are proportional to the imaginary part of the Raman susceptibility.

The "B_{2g} spectra" and "B_{1g} spectra" presented below are actually from the linearly-polarized light scattering geometries of XY (B_{2g} + A_{2g}) and X'Y' (B_{1g} + A_{2g}), respectively. The A_{2g} contribution to these spectra was determined from the sum of XY and X'Y' spectra minus the spectrum obtained in LR (B_{1g} + B_{2g}) circularly-polarized scattering geometry. A_{2g} was found to be negligible.

FIG. 2: Isotope dependance of the the "2Δ-like" peaks in Raman spectra measured at 6 K. a) B_{2g} peaks of B10-Y (thick line) and B11-Y (thin line), b) B_{2g} peaks of B10-Lu (thick line) and B11-Lu (thin line), c) A_{1g} peaks of B10-Y (thick line) and B11-Y (thin line), d) B_{1g} peaks of B10-Y (thick line) and B11-Y (thin line).

no such isotope dependence is observed. On the contrary, the B_{1g} peak tends to show a positive isotope effect, but the greater breadth of the peak hinders determining an isotope effect within experimental resolution.

In our earlier paper,[10] it was shown that the B_{2g} peak follows the BCS prediction for the temperature dependence of the superconducting gap. However, as seen in Fig.2a, it does not follow the BCS prediction for the isotope dependence of the gap. Rather, the B_{2g} peak frequency in YNi_2B_2C, as well as the leading edge of the peak, exhibits a negative isotope effect. There are prior reports of some of these experimental results.[12]

We found empirically that in the region of the 2Δ peaks the ratio of B_{2g} to B_{1g} Raman intensities can be fit to a Lorentzian expression

$$\frac{I_{B_{2g}}}{I_{B_{1g}}} = \frac{A}{(\omega - \omega_0)^2 + \Gamma^2}. \qquad (1)$$

near the 'gap-like' peak frequency, ω_0.

Figure 3 shows the results of fitting the above equation to the ratio of the B_{2g} to B_{1g} spectra. The fit is excellent around the peak and below, deviating much at higher frequencies. No such fit is possible for $I_{B_{2g}}$ or $I_{B_{1g}}$ itself. From the fits to several sets of B_{2g}/B_{1g} Raman ratios, we obtained the isotope effect exponent due to boron, $\alpha_B^{Raman} = -0.32 \pm 0.03$ for YNi_2B_2C and -0.04 ± 0.07 for $LuNi_2B_2C$, where $\alpha_B^{Raman} \equiv -\frac{\Delta \ln \omega_0}{\Delta \ln M_B}$. M_B is the mass of the boron isotopes. Since there is little evidence for an isotope effect in the B_{1g} spectra, we attribute these results for α_B^{Raman} primarily to the negative isotope effect on the B_{2g} spectrum.

FIG. 4: Plot of B_{2g} peak frequencies (Ω) at 6K and the onset temperatures of the superconducting transition of six different YNi_2B_2C single crystals. The dashed line on the plot represents BCS prediction $2\Delta_0 = 3.52k_BT_c$.

We have measured the superconducting transition temperatures using a SQUID magnetometer and eliminated the possibility that the particular B10 samples in our study have lower T_c values than those of B11 samples. Figure 4 shows a plot of B_{2g} peak frequencies (Ω) at 6K and the onset temperatures of the superconducting transition of six different YNi_2B_2C single crystals. As is clearly seen, B11-Y samples do have *larger* B_{2g} peak frequencies than B10-Y samples, in contradiction to the BCS prediction. This figure shows that the isotope effect of the B_{2g} peak frequencies is *negatively* correlated with the isotope effect of the T_c in YNi_2B_2C. The dashed line on the plot represents $2\Delta_0 = 3.52k_BT_c$, the BCS prediction in the weak coupling limit.

There is no previous report known to us of an observed negative isotope effect of the superconducting gap. Negative isotope effects have been observed for the transition temperatures of the Pd-H(D) system[13] and underdoped $YBa_2Cu_3O_{7-\delta}$.[14] In the following discussion we assume that the B_{2g} peak is directly due to superconducting gap 2Δ. How, then, can we explain a negative isotope effect for the gap measured in B_{2g} Raman symmetry along with a positive isotope effect for T_c and small or zero isotope effects for the gap measured in B_{1g} and A_{1g} symmetries?

The most likely possibility is that the boron portion of the electron-phonon interaction plays out quite differently on the various portions of the Fermi surface. It would be necessary for the B_{2g} Raman vertex to probe those parts of the Fermi surfaces which have a negative boron-isotope effect on the value of the gap. Correspondingly, the isotope effect would have to be much smaller and possibly positive on those parts of the Fermi surface probed in A_{1g} and B_{1g} Raman geometries.

There is a simple picture of the electronic structure that may give a strong clue to where the B_{2g} vertex is large. According to the band structure calculations for $LuNi_2B_2C$[15, 16] and YNi_2B_2C,[17] there is a flat band that may cross the Fermi surface near the X point [wavevector given by $(\pi/a, \pi/a, 0)$]if there is a small change in parameters. This band has strong anti-bonding $dd\sigma$ interactions as well as d_{z^2} character on Ni sites.[16] If we take a nearest neighbor, planar, Ni-Ni tight binding model with coupling t, we obtain a band dispersion $\varepsilon(k) = 4t\cos(k_xa/2)\cos(k_ya/2)$. This has a saddle point at X. A good starting approximation to the Raman vertex is the so-called mass approximation, valid when the photon energy is less than that of all interband transitions starting or ending at the Fermi energy. It says that the B_{2g} Raman vertex is proportional to $\partial^2\varepsilon/\partial k_x\partial k_y$. For the assumed band structure, this would give $\partial^2\varepsilon/\partial k_x\partial k_y = 4t(a/2)^2\sin(k_xa/2)\sin(k_ya/2)$, which takes on its maximum value at the X point.

It would be useful to verify this suggestion with a band structure calculation of the mass vertex of the band that crosses the Fermi energy near the X point. The next step would be to study the coupling between this band and the boron phonon modes. There is one such calculation in the literature, which emphasizes the role of the A_{1g} zone center boron mode on modulating the angle of the B-Ni-B tetrahedra. [18] However, much more needs to be done, with a particular look for novel couplings that would give a negative isotope effect on the gap associated with this band.

The superconducting gap of borocarbides will not be as simple as calculated by BCS theory. The finite intensity below the gap observed in our Raman measurements (Figs. 1 and 2 and[10]), a nearly T^3 behavior of the electronic specific heat,[19] and evidence of small gap on the small pocket Fermi surface from de Haas-van Alphen measurements[20] of superconducting RNi_2B_2C (R = Y, Lu) system are good indications of the complex nature

of the gap of borocarbide superconductors.

In conclusion, we observed a negative boron isotope effect of the gap-like feature in B_{2g} electronic Raman spectra from YNi_2B_2C single crystals. For $LuNi_2B_2C$, the negative isotope effect is weaker, and may be zero within our experimental resolution. A likely explanation is that the B_{2g} Raman vertex selectively probes those portions of the Fermi surface which show a negative boron-isotope effect of the order parameter in the superconducting state. We have suggested that this may occur at the X point, the corner of the Brillouin zone in the basal plane.

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